Measurement of Uranium Isotopic Composition with High Sensitivity and Specificity by Secondary Ion Mass Spectrometry

NIST recently acquired a SIMS instrument that offers the possibility of distinguishing an isotope of interest from a potentially interfering species through improved mass spectral resolution. One limitation of SIMS is the existence of mass spectral interferences that are combinations of atoms of different elements forming an ion with the same nominal mass as an isotope of interest. The purpose of this study was to define the instrumental conditions to achieve this separation while minimizing the effect on ion transmission. An instrument and a set of procedures that can realize these results will benefit organizations associated with nuclear forensics through increased reliability of uranium isotopic data.

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Uranium that is highly enriched in the isotope ^{235}U is a key component of one type of fission-based atomic weapon. Therefore, the measurement of the isotopic composition of uranium is of keen interest to nuclear forensics investigators from organizations such as the International Atomic Energy Agency (IAEA). The IAEA carries out environmental sampling at facilities in its member states with the goal of detecting undeclared uranium enrichment activity. The collected samples are subjected to various screening measurements, the most important of which is the determination of the uranium isotopic composition in the material that is usually in the form of particles distributed on cloth wipes.

Secondary ion mass spectrometry (SIMS) is an effective isotopic measurement method for this purpose because of its ease of sample preparation, sensitivity, and capability to locate uranium-bearing particles among background debris in an automated search mode.

NIST has played a significant role in developing and testing SIMS methods for uranium isotopic measurements, and in transferring this capability to the IAEA Safeguards Analytical Laboratory in Austria.

A series of measurements of the uranium mass spectral peak shape from a uranium oxide isotopic reference material were made at different combinations of entrance and exit slit settings that control the mass resolving power and peak shape, but also affect the secondary ion transmission. The results of some of these measurements are shown in Table 1 and Figure 1. The conditions of the first row correspond to 100 % transmission of uranium ions through the mass spectrometer, the conditions of successive rows correspond to narrower peak shapes, but with some reduction in ion transmission.

Slits (µm)	*Relative Transmission*	*MRP @ 10 %*	*Rel.Tail Sig. @ ^{235}U*
588/350	1.00	2520	**8.8×10^{-5}**
250/350	0.98	2540	**1.2×10^{-5}**
180/350	0.85	2600	**$<1.0\times10^{-5}$**
150/300	0.76	3080	**$<1.0\times10^{-5}$**

Table 1. ***Relative ion transmission and mass resolving power for ^{235}U peak at various entrance/exit slit settings. Last column is relative contribution of peak tail at ^{235}U mass position if peak is shifted to ^{208}Pb^{27}Al mass position to simulate mass spectral interference.***

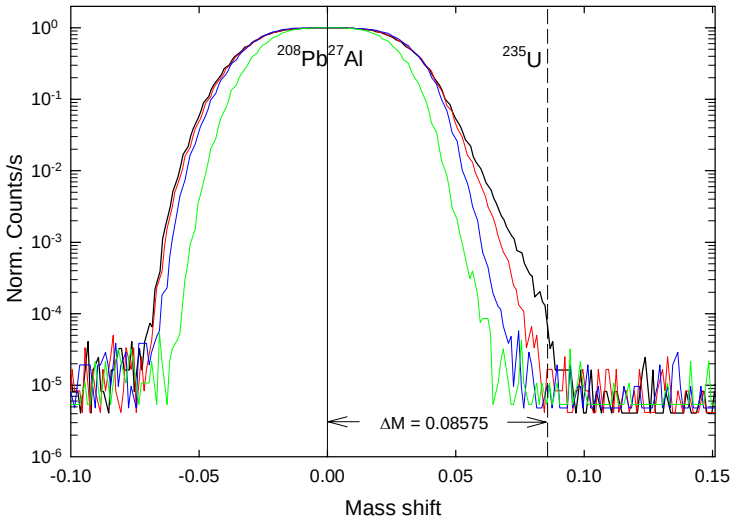

Figure 1. ***Peak shapes of ^{235}U for slit settings shown in Table 1, shifted to mass position of ^{208}Pb^{27}Al to show peak tail contribution at ^{235}U mass position. The black, red, blue, and green traces correspond to the slit settings of rows 1-4 in Table 1, respectively.***

Reliable isotopic abundance measurements require that potential mass spectral interferences should make an insignificant contribution. A calculation of the exact masses of all possible ion combinations shows that lead-containing molecular ions are the most closely spaced potential interferences to the uranium isotopes at m/z 234, 235, 236, and 238. An example is the $^{208}Pb^{27}Al$ ion that would be centered 0.08575 mass units below the ^{235}U mass position. To demonstrate the degree of rejection of this peak, should it occur, the ^{235}U peak shapes were used to simulate PbAl at its mass position so the contribution of the interfering peak tail at the ^{235}U mass position could be calculated. This procedure is shown graphically in Fig. 1 and numerically in the last column of Table 1. The conclusion from these studies is that a rejection of this worst-case spectral interference by a factor of 10^5 can be achieved with an insignificant reduction in ion transmission by appropriate instrumental settings.

Future Plans:
Additional studies of uranium ionization efficiency and isotopic measurement protocols are expected to further improve the measurement of uranium isotopic composition in small particles by SIMS.